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IGNITION OF SIMULATED PROPELLANTS  
BASED ON AMMONIUM PERCHLORATE\*\*

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BASED ON AMMONIUM PERCHLORATE**

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**ABSTRACT**

The ignitability of simulated solid propellants based on  $\text{NH}_4\text{ClO}_4$  has been studied using the radiation from an arc image furnace as a source of ignition energy. The experimental measurements provide (for given conditions) the minimum time of exposure to radiation required for ignition and combustion of pellets pressed from powdered mixtures of:  $\text{NH}_4\text{ClO}_4$  and copper chromite;  $\text{NH}_4\text{ClO}_4$ , carbon, and copper chromite; and  $\text{NH}_4\text{ClO}_4$ , copper chromite, and polyethylene. Minimum exposure times were determined as a function of pellet composition, flux (20 to 120 cal/cm<sup>2</sup> sec), pressure (1 to 40 atm), and composition of the atmosphere ( $\text{N}_2$ , He, A) in contact with the pellet.

The experimental results in conjunction with supplementary kinetic information indicate that, for these materials, gas phase ignition neednot be preceded by a catastrophic rate of heat release within the sample. The critical chemical species involved during gas phase ignition is probably perchloric acid. Under some circumstances, a high rate of solid reaction does appear to be involved during ignition of the materials.

## I. INTRODUCTION

Ignition is a complex process which involves initial attainment of a thermally unstable state, growth of chemical reaction, appearance of a visible flame, and spreading of the flame over the exposed surface of the propellant.

If supplied sufficient energy, any chemical system capable of exothermic reaction will reach such a thermally unstable state, and subsequent chemical reaction will lead to ignition or explosion. The nature of the unstable state depends on the energy supply rate, amount of energy supplied, ambient conditions, and the chemical reactions responsible for ignition. Obviously, considerable study will be required to identify the ignition reactions, to determine the conditions under which each contributes significantly to the over-all process, and to establish the role played by each propellant ingredient.

For solid propellants based on  $\text{NH}_4\text{ClO}_4$ , identification of the ignition reactions is difficult. The propellant may contain, besides  $\text{NH}_4\text{ClO}_4$ , an organic binder, a burning rate catalyst, and powdered aluminum. In such mixtures the possible reactions are many.  $\text{NH}_4\text{ClO}_4$ , itself, is unstable at moderate temperatures and can decompose with the evolution of heat and chemically reactive gases, and its decomposition is affected by burning rate catalysts such as copper chromite.  $\text{NH}_4\text{ClO}_4$  also can dissociate<sup>1</sup> to  $\text{NH}_3$  and  $\text{HClO}_4$ , the latter a reactive, unstable gas. The binder may degrade or may react with  $\text{NH}_4\text{ClO}_4$  or its decomposition products. If powdered aluminum is present, it too may participate in the ignition reactions. Finally, the course of reaction during ignition may depend on the composition and pressure of the atmosphere in contact with the propellant.

Experimental studies\* aimed at a detailed knowledge of the ignition of propellants based on  $\text{NH}_4\text{ClO}_4$  have differed mainly in the means of energy supply. The principal means employed have been:

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\* Ref. 2 is a recent review of such studies.

1. Conductive heat transfer from an electrically heated wire in contact with the sample<sup>3,4</sup>
2. Conductive and convective heat transfer from a hot atmosphere<sup>5-8</sup>
3. Absorption of radiant energy.<sup>9-11</sup>

The experimental conditions of these studies have differed considerably, particularly in the rate of energy supply, and in the pressure, composition, and temperature of the atmosphere in contact with the propellant. The conclusions drawn from these studies have also differed: Ignition has been attributed to heat release within the propellant,<sup>3,9</sup> to attack of the binder by the decomposition products of  $\text{NH}_4\text{ClO}_4$ ,<sup>12</sup> and to unidentified vapor phase reactions.<sup>10,11</sup>

The present study was undertaken to establish--for simulated propellants simpler in composition than real propellants--empirical relations between ignitability and the following experimental variables: the rate of energy application, the pressure and composition of the atmosphere in contact with the propellant, and the composition of the propellant itself. These relations can then be used to derive values of such quantities as the surface temperature of the propellant during exposure to energy in the absence of reaction. Such data are required to evaluate plausible reaction mechanisms and the role played by each propellant ingredient.

In the absence of supplementary kinetic information, only qualitative conclusions can be drawn from ignitability data. Consequently, our approach to the problem, similar to the approach in Ref. 11, has been to obtain (where possible) the kinetic information required for analysis of propellant ignitability. By selecting chemically simplified propellants the reaction possibilities are decreased, and the problem becomes more tractable.

## II. EXPERIMENTAL

### A. Materials

Propellant samples, pellets 0.3" in diameter and ~ 3 mm thick, were prepared by pressing powder mixtures hydraulically at ~ 70,000 psi. The powder mixtures consisted of  $\text{NH}_4\text{ClO}_4$  (AP), copper chromite (CC), carbon black (C), and polyethylene (PE). The ammonium perchlorate, from a single batch of crystalline  $\text{NH}_4\text{ClO}_4$  (Matheson-Coleman-Bell, Reagent Grade), was dried at ~ 100°C, then ball-milled in a small laboratory mill, and sieved into four fractions:  $d < 43\mu$ , 43 to 61 $\mu$ , 61 to 88 $\mu$ , and 88-124 $\mu$ ; the fractions were mixed as desired. The copper chromite was Harshaw Chemical Company Cu-0202-p powder with a nominal particle size of about 3½ $\mu$ . The carbon black was Cabot, Incorporated, furnace black, type Sterling VR, with a nominal particle size of 50 m $\mu$ . Powdered polyethylene, Grade 6A, was obtained from Allied Chemical Corporation. Powder mixtures were first dispersed by shaking and then lightly ground with mortar and pestle to deagglomerate and to complete the dispersion.

Pellet properties of importance in the present study are density, heat capacity, thermal conductivity, and optical absorptivity. The first three are primarily determined by the properties of  $\text{NH}_4\text{ClO}_4$ , the major ingredient in all samples. The last depends on the minor constituents of the mixture. The pellet densities were determined from pellet weight and dimensions. For pure  $\text{NH}_4\text{ClO}_4$ , pellet density is 97-98% of theoretical density. Specific heat data and optical absorptivity data are available from Ref. 11, and thermal conductivity data from Ref. 13.

### B. The Arc Image Furnace

The present study of propellant ignitability utilizes an arc image furnace as a source of ignition energy. The use of such a furnace and its associated apparatus has a number of advantages: The composition and pressure of the atmosphere in contact with the propellant is easily controlled, and the short time scale associated with a high rate of energy application (up to ~ 120 cal/cm<sup>2</sup> sec) permits a relatively simple

mathematical analysis of the data. The main disadvantages are: The propellants must be strong absorbers of visible light; the atmosphere in contact with the propellant is cold. The furnace itself, described in detail in Ref. 10, provides an intense beam of light with wave lengths between 0.2 and  $2\mu$  and a maximum intensity at about  $1/2\mu$ . The beam converges in a 120-degree vertex angle cone to a roughly ellipsoidal image with axes of approximately 1 cm. A propellant pellet, inside a 1.26-cm internal diameter Pyrex cylinder, is positioned within this image so that one face is exposed to radiation, with the maximum flux near the center of the pellet face. By conventional means the pressure within the cylinder can be varied from 1 to 40 atm. A gas stream ( $N_2$ , He, or A) flows through the cylinder at a rate of about 50 cc/min (STP). The flux at the sample face can be varied from 20 to 120 cal/cm<sup>2</sup> sec by mechanically blocking part of the beam. Exposure time of the pellet to the beam is controlled by adjusting the rotational speeds of three concentric slotted discs (see Fig. 1).

The two important experimental quantities in an arc image study are flux at the sample face and the time of exposure to that flux. Determination of each involves the flux-calibrating calorimeter described in detail in Ref. 14. The sensing element of the calorimeter is a blackened spherical segment partially shielded from the beam by a thin silver sheet containing a small circular aperture. The calorimeter is so designed that the shield occupies the same position with respect to the beam as the front surface of an ignition sample. Radiation passing through the aperture in the shield is absorbed by the detector causing a temperature rise, which is measured by a thermocouple attached to the back surface of the detector. During calibration the thermocouple signal is recorded and the average absorbed flux is calculated from the rate of temperature rise, the area of the aperture, and the mass and heat capacity of the detector. The time of exposure was usually about 100 to 200 msec and the temperature rise of the detector from 25 to 50°C.

All calibrations were carried out using a 0.1" aperture. Calibration records for apertures of various diameters in the range from  $d = 0.05"$  to  $d = 0.20"$  revealed that the rate of temperature rise of the detector involves not only the amount of absorbed radiant energy but also heat losses by the detector to its surroundings and heat gains by conduction from the shield which itself is heated by the intercepted part of the beam. It is this feature that is responsible for the apparent dependence of flux on aperture size.<sup>14</sup> For aperture diameters less than 0.1", heat gain from the shield is greater than heat loss. For diameters greater than 0.1", loss exceeds gain. For a diameter of 0.1", loss and gain are nearly equal.

The calorimeter measures absorbed flux. Incident flux was calculated on the basis of a detector absorptivity of 0.83. A comparative study of seven different calorimeters including ours at the Naval Ordnance Test Station (China Lake, Calif.) indicated that the previously used value of 0.97 obtained from Ref. 11 was high. To establish the absorptivity, the absorbed flux was measured after the calorimeter detector had been lightly coated with acetylene black and compared with the absorbed flux by the uncoated detector. If the absorptivity of the coated detector is assumed to be one, then the cited comparison indicates that the absorptivity of the uncoated detector is 0.83.

Sample exposure time to the flux is inversely proportional to the speed of the fastest of the three rotating discs shown in Fig. 1. The constant of proportionality, however, depends on the effective size of the image in the plane of the disc. The constant of proportionality was determined by using a low, known rate of disc revolution and the recorded response of the calorimeter to give the duration of the corresponding pulse. Such records revealed that the pulse is very nearly square and that the pulse duration corresponds closely to that expected for a point image in the plane of the disc. All our exposure times for actual ignition measurements are based on the constant of proportionality determined (as described above) and are 30% lower than those previously reported

(Ref. 11). Any comparison between the two studies must take this difference into account, as well as the different values used for detector absorptivity.

### C. Experimental Procedure

For experimental purposes ignitability of a propellant may be defined as the inverse of the minimum time of exposure of the propellant to a constant radiant flux that will result in ignition and combustion of the propellant. The desired quantity, the minimum exposure time  $\tau$ , is determined in the following way. For a fixed value of incident flux, and a given pressure and atmosphere a pellet of chosen composition is exposed to radiant energy for a length of time thought sufficient to cause ignition. If the exposure time is not long enough to cause ignition, another pellet of the same composition is exposed for a longer time, etc. If exposure results in ignition, another pellet is exposed to a pulse of shorter length, etc. Proceeding in this manner, one can usually establish the minimum time with a precision of  $\pm 5\%$ . The procedure can then be repeated for other values of the controllable variables. No measurement was made of the elapsed time between the end of the pulse of minimum length and the appearance of flame. However, the surface temperature of an unreactive material which has been heated by light absorption decays very rapidly after exposure, and the rate of decay can be calculated.<sup>14</sup> For our samples, in the absence of reaction, the surface temperature will drop to 80% of the value at the end of the exposure period in a time equal to 5% of the original pulse length. Consequently ignition, if it is to occur, must occur in a time small compared to the original pulse length.

For a given set of conditions the experimental data consist of (1) the pellet properties, (2) the average incident flux  $\Phi$  measured by the calorimeter, (3) the pressure and composition of the atmosphere in contact with the pellet, and (4) the minimum time  $\tau$  of exposure to the flux  $\Phi$  that is required for ignition and combustion of the pellet.

These data are then used to calculate (1) the maximum flux to which any part of the pellet face is exposed, (2) the fraction of that flux which is absorbed by the sample, (3) the maximum energy absorbed by the pellet per unit area of pellet surface, and (4) the maximum surface temperature  $T_s$  in the absence of reaction at the end of the exposure period.

Calculation of the maximum absorbed flux  $\dot{\Phi}_m$  involves three quantities: the ratio of the maximum flux at the focus of the arc image beam to the average flux measured by the calorimeter, the pellet absorptivity, and heat losses from the pellet surface to the surrounding atmosphere. Previous study<sup>14</sup> indicated that the maximum flux is 5% greater than the average. The absorptivity<sup>11</sup> of samples containing copper chromite but no carbon is 0.95. The absorptivity<sup>11</sup> of samples containing carbon is 0.98. The amount of heat loss during irradiation by conduction from the propellant to the ambient gas is about 2% of the flux incident on the sample in a  $N_2$  or A atmosphere and about 4% of the incident flux in a He atmosphere. Given  $\dot{\Phi}_m$ , the maximum energy,  $\dot{\Phi}_m \tau$  (cal/cm<sup>2</sup>), absorbed by the pellet is readily calculated.

From the cited experimental data one can calculate  $T_s$ , the propellant surface temperature in the absence of reaction at the end of the exposure of the sample to radiant energy. For this calculation the propellant pellet is regarded as an unreactive, perfectly absorbing, homogeneous, semi-infinite slab on which is incident a constant uniform flux  $\dot{\Phi}_m$ . Microscopically, the sample is in fact distinctly inhomogeneous. Some consequences of this inhomogeneity have been discussed.<sup>11</sup> However, on a macroscopic scale the pellet is effectively semi-infinite and the heat flow is one-dimensional for times of the length we are considering.<sup>11</sup> Accordingly,  $T_s$  can be calculated using the expression<sup>17</sup>

$$T_s - T_i = \frac{2\dot{\Phi}_m}{(\lambda c_0)^{1/2}} \left( \frac{\tau}{\pi} \right)^{1/2} \quad (1)$$

where  $T_i$  = the initial sample temperature ( $^{\circ}C$ )

$T_s$  = surface temperature at time  $\tau$  ( $^{\circ}C$ )

$$\begin{aligned}\dot{q}_m &= \text{radiant flux (cal/cm}^2 \text{ sec)} \\ (\lambda c \rho)^{\frac{1}{2}} &= \text{an average "thermal responsivity" (cal/sec}^{\frac{1}{2}} \text{ deg cm}^2 \text{ of the pellet)}\end{aligned}$$

Thermal responsivity involves  $\lambda$ , the pellet thermal conductivity,  $c$ , the pellet heat capacity, and  $\rho$ , the pellet density. For our propellants,  $T_s$  is greater than  $240^\circ\text{C}$ , the crystal transition temperature. Consequently, we used for  $\lambda$  an average value between  $T_i$  ( $\sim 25^\circ\text{C}$ ) and  $240^\circ\text{C}$  for pure  $\text{NH}_4\text{ClO}_4$  pellets ( $\lambda = 1.02 \times 10^{-3} \text{ cal cm}^{-1} \text{ sec}^{-1} \text{ deg}^{-1}$ ). The thermal conductivity of  $\text{NH}_4\text{ClO}_4$  at temperatures greater than  $240^\circ\text{C}$  is not known. The density  $\rho$  is the measured value of the pellet at room temperature. The heat capacity  $c$  is an effective average value for  $\text{NH}_4\text{ClO}_4$  between  $T_i$  and  $T_s$  and includes the heat of transition when  $T_s > 240^\circ\text{C}$ . In all cases  $(\lambda c \rho)^{\frac{1}{2}}$  is about  $2.6 (\pm 0.1) \times 10^{-2} \text{ cal/sec}^{\frac{1}{2}} \text{ deg cm}^2$ . The possible error associated with the change in crystal density at  $T = 240^\circ\text{C}$  has been ignored.

### III. EXPERIMENTAL RESULTS

#### A. $\text{NH}_4\text{ClO}_4/\text{CC}$ Ignition

Particle size of  $\text{NH}_4\text{ClO}_4$  in a composite propellant is known to affect combustion and might affect ignitability. This possibility was investigated using various AP/CC samples containing 5 wt % CC. The minimum exposure time required for ignition in a  $\text{N}_2$  atmosphere was measured for six different mixtures, a fixed incident flux, and at various pressures in the range from 25 to 40 atm. The results of the measurements are shown in Table I. The flammability limit, the minimum pressure at which stable combustion is possible, appeared to vary slightly with particle size distribution but is about 25 atm for all mixtures. At pressures above this limit the exposure time is independent of pressure. The exposure times in the table are average values in the cited pressure range. The slight dependence of exposure time on particle size distribution is of the same order as the experimental error and is not

significant. For the experimental conditions listed in Table I, it may be concluded that ignitability does not depend on  $\text{NH}_4\text{ClO}_4$  particle size.

The CC content of an AP/CC pellet affects the burning rate and the flammability limit of the pellet.<sup>18</sup> For the conditions shown in Table II, CC content does not affect ignitability. The lower flammability limit increases with decreasing CC content; this explains the variation in pressure range shown in Table II.

A systematic study of the ignitability of AP/CC (95 wt %/5wt %) pellets was made using Mixture A (see Table I). A high CC content was used in order to avoid undue difficulty with flammability limits. The choice of AP mixture was arbitrary but experimentally convenient. Two inert atmospheres ( $\text{N}_2$  and He) were used, four values of incident flux, and various pressures in the range from 25 to 40 atm. In He, as in  $\text{N}_2$ , the flammability limit is about 25 atm. For all fluxes used, and in both  $\text{N}_2$  and He atmospheres, the minimum exposure time is independent of pressure in the cited range but differs markedly for the two atmospheres. For convenience, the experimental data are shown in Fig. 2 in the form  $\bar{\Phi}_m \tau$  as a function of  $1/\bar{\Phi}_m$ . As noted earlier,  $\bar{\Phi}_m$  is the peak flux corrected for sample reflectivity and heat loss to the surrounding gas. The experimental exposure time,  $\tau$ , is an average value in the pressure range from 25 to 40 atm. As shown in Fig. 2, the results can be expressed in the form

$$(\bar{\Phi}_m \tau)_{\text{N}_2} = \frac{48}{\bar{\Phi}_m} + 0.64 \quad (2)$$

$$(\bar{\Phi}_m \tau)_{\text{He}} = \frac{66}{\bar{\Phi}_m} + 1.27 \quad (3)$$

Frequently, ignitability data<sup>8,9</sup> are presented in the form

$$(\tau)^{\frac{1}{2}} = a(\bar{\Phi}_m)^{-b} \quad (4)$$

Our data can be fitted by such expressions with  $b = 0.8$  for both  $\text{N}_2$  and He. The experimental data have also been used to calculate, by

means of Eq. (1), the surface temperature,  $T_s$ , which would be reached at time  $\tau$  in the absence of chemical reaction. The variation of  $T_s$  with  $\dot{q}_m$  is shown in Fig. 3.

#### B. $\text{NH}_4\text{ClO}_4/\text{CC}/\text{C}$ Ignition

As previously noted,<sup>11</sup> pellets prepared from mixtures of AP, CC, and C are unusually ignitable. One such mixture containing 95 wt % AP, 2½ wt % CC, and 2½ wt % C was selected for detailed study. Some results for an incident peak flux of 85 cal/cm<sup>2</sup> sec are shown in Fig. 4. The effect of gas composition is pronounced. In  $\text{N}_2$  the minimum exposure time appears to be sensitive to pressure at low pressures ( $p < 20$  atm), but not at high pressures ( $p > 20$  atm). The variation of  $\tau$  with  $\dot{q}_m$  for a fixed pressure of 35 atm was determined in nitrogen and in helium. The helium data tended to be erratic. For  $\text{N}_2$ , however, the quantity  $\dot{q}_m \tau$  varied as

$$(\dot{q}_m \tau)_{\text{N}_2} = \frac{20}{\dot{q}_m} + 0.27 \quad (5)$$

The variation of surface temp with flux is shown in Fig. 5. As with AP/CC (95/5),  $\tau^{1/2}$  is proportional to  $(\dot{q}_m)^{-0.8}$  in a  $\text{N}_2$  atmosphere. The less accurate helium data are consistent with such an expression.

#### C. $\text{NH}_4\text{ClO}_4/\text{CC}/\text{PE}$ Ignition

AP/CC mixtures and AP/CC/C mixtures differ from real propellants primarily in the absence of an organic fuel. Carbon is a fuel but a rather unique one. The possible influence of an organic fuel on ignitability was investigated using pellets prepared from powdered polyethylene and the 95/5, AP/CC, Mixture A. Three compositions were used containing 4, 8, and 12 wt % polyethylene, respectively. We measured  $\tau$  as a function of flux, pressure, atmosphere composition, and PE content.

Some experimental results for PE-containing pellets are shown in Fig. 6. In a  $\text{N}_2$  atmosphere the required exposure times for the mixture containing 4 wt % PE are the same as those for AP/CC (95/5) except that independence of pressure extends now to 15 atm. The abrupt increase

in  $\tau$  for  $p_{N_2} < 15$  atm is probably associated with proximity to the flammability limit. For mixtures containing 8 wt % PE, in a  $N_2$  atmosphere,  $\tau$  is nearly the same as for AP/CC for pressures less than 30 atm. There is an apparent pressure dependence above 30 atm which must be associated with polyethylene. A high PE content (12 wt %) clearly increases ignitability in a  $N_2$  atmosphere. The results suggest that in  $N_2$  the properties of the AP/CC mixture determine ignitability except at high pressure or a high PE content. The results further suggest that the processes involved in the ignition of AP/CC (95/5) pellets are independent of pressure in the range from 1 to 40 atm.

As shown in Fig. 6, the presence of PE (8 wt %) does reduce the required exposure time in a helium atmosphere. As with other mixtures, the composition of the ambient atmosphere affects ignitability, although the effect of substituting He for  $N_2$  is less marked for the PE mixture than for AP/CC (95/5) itself.

The dependence of  $\tau$  on  $\phi_m$  was determined at a fixed pressure of 35 atm using Mixture P8, in  $N_2$  and in He. The best results were obtained with  $N_2$  for which

$$(\phi_m \tau)_{N_2} = \frac{29}{\phi_m} + 0.67 \quad (6)$$

and

$$\tau^{\frac{1}{2}} \propto \phi_m^{-\frac{3}{4}}.$$

The variation of calculated surface temperature with  $\phi_m$  is shown in Fig. 7. At this high pressure (35 atm) the presence of PE clearly affects the ignitability of the mixture.

#### D. Supplementary Kinetic Information

As noted earlier, CC promotes the decomposition of  $NH_4ClO_4$  and this is one possible role played by CC during ignition. To evaluate this possibility, it is necessary to have quantitative kinetic data in a mathematical form which permits extrapolation to ignition temperatures.

Accordingly, we measured the rate of decomposition of several AP/CC mixtures by means of an adiabatic method. The complete results of this study will be reported at a later date. For some mixtures the rate of decomposition could not be simply expressed. However, usable results were obtained for AP/CC (95/5) wafers pressed from  $\text{NH}_4\text{ClO}_4$  powder with particle sizes in the range from 43 to 61 $\mu$ . We found that for such samples the rate of temperature rise under adiabatic conditions in the temperature range from 240 to 325°C is described by the expression

$$\left(\frac{dT}{dt}\right)_{\text{ad}} = 10^{16.9} e^{-44,000/RT} \text{ deg/sec} \quad (7)$$

Equation (7) is a form conveniently extrapolated to ignition temperatures.

Apparatus developed to study the adiabatic decomposition of  $\text{NH}_4\text{ClO}_4$  was adapted to provide a kind of thermal history of wafers prepared from some of the compositions used in the arc image study. This information, although qualitative, does provide an "ignition temperature" which is not the result of calculation, in contrast to the arc image "ignition temperatures."

A history was obtained in the following way. About five grams of powder was pressed hydraulically at about 25,000 psi into a wafer 1 $\frac{1}{8}$ " in diameter and about 4 mm thick. The wafer was then clamped between two aluminum blocks which could be electrically heated. Starting from room temperature, the two block temperatures were increased at a rate of 5 to 10 deg/min. By means of two chromel-alumel thermocouples, one inserted into a hole in one block, the other inserted into a hole in the sample, the block temperature and the temperature difference between the block and the center of the wafer were measured up to the time of ignition. Wafers of these compositions were used: AP/CC (95/5), AP/CC/C (95/2 $\frac{1}{2}$ /2 $\frac{1}{2}$ ), AP/C (97 $\frac{1}{2}$ /2 $\frac{1}{2}$ ), and AP/CC:PE (95/5:12).

From a number of such histories we found that:

1. Heat release is not detectable at temperatures below the crystal transition at 240°C.

2. In all cases heat release within the sample is detectable prior to ignition.
3. Ignition occurs (visible flame) abruptly ( $T > 240^{\circ}\text{C}$ ) without being preceded by a catastrophic rate of solid reaction.

At a heating rate of  $\sim 5$  deg/min, the AP/CC, AP/CC:PE, and AP/C wafers all ignited at a wafer temperature of about  $300^{\circ}\text{C}$ . The AP/CC/C wafers ignited at about  $275^{\circ}\text{C}$ . These ignition temperatures depend on system variables. In particular, ignition temperature increases with increasing heating rate. The results do reveal that AP/CC/C is more ignitable than the other compositions and that for all mixtures gas phase ignition is not a consequence of runaway decomposition. A pure AP wafer will decompose but not ignite when treated as above.

#### IV. DISCUSSION

##### A. $\text{NH}_4\text{ClO}_4/\text{CC}$ and $\text{NH}_4\text{ClO}_4/\text{CC}/\text{PE}$ Ignition

For both AP/CC and AP/CC/PE mixtures the dependence of  $\tau$ , the minimum exposure time, on gas composition suggests that in  $\text{N}_2$  or A at high pressure, gas phase reactions or heterogeneous reactions involving normally gaseous species control the early stages of the ignition processes. No immediate conclusions can be drawn regarding ignition in a He atmosphere. Two observations suggest that the thermal conductivity of the gas is the physical property responsible for the dependence of  $\tau$  on gas composition. These are, first, that  $\tau$  varies in the order  $\tau(\text{He}) > \tau(\text{N}_2) > \tau(\text{A})$  and, second, that  $\tau$  is independent of pressure. It should be noted that with this interpretation, independence of pressure does not imply that solid phase reactions control ignition. These general conclusions are consistent with the results of the thermal history measurements.

The cited qualitative conclusions refer to both to mixtures containing PE and those which do not. The principal ignition promoter under our experimental conditions is copper chromite. Few conclusions

can be drawn regarding the role played by PE during ignition and the subsequent burning of the sample. The principal one appears to be simply as a fuel. In  $N_2$  a low PE content (4%) merely lowers the flammability limit. The exposure time is the same as for AP/CC pellets alone. A higher PE content (8%) lowers the flammability limit even more but only increases ignitability compared to AP/CC pellets at high pressure. A high PE content (12%) definitely increases ignitability compared to AP/CC. In helium, an 8% PE content also increases ignitability by an unidentified mechanism.

The validity of the conclusions regarding the ignitability of AP/CC pellets can be supported by means of the kinetic data represented by Eq. (7). That data represent the adiabatic rate of temperature rise resulting from the decomposition of a solid AP/CC sample. If heat release from solid decomposition is important during the early stages of ignition, then one would expect  $\left(\frac{dT}{dt}\right)_{ad}$ , evaluated at the surface temperature  $T_s$  (see Fig. 3), to be comparable with the rate of temperature rise  $\left(\frac{dT}{dt}\right)_{ig}$  derived from Eq. (1) and evaluated at the end of the exposure period  $t = \tau$ . Application of this procedure to the results of a theoretical analysis of propellant ignition<sup>19</sup> indicated that  $\left(\frac{dT}{dt}\right)_{ad}$  is about  $2\frac{1}{2}$  to 3 times as great as  $\left(\frac{dT}{dt}\right)_{ig}$  when ignition is a consequence of a catastrophic rate of solid reaction. The results of this procedure when applied to our AP/CC data are shown in Fig. 8 and indicate that solid decomposition is responsible for ignition in a helium atmosphere. The  $N_2$  data indicate that solid decomposition does occur in a  $N_2$  atmosphere but not at a rate sufficiently great to dominate the ignition process except possibly at very high flux.

The apparent increase in the ratio  $\left(\frac{dT}{dt}\right)_{ad} / \left(\frac{dT}{dt}\right)_{ig}$  with increasing flux shown in Fig. 8 may be spurious. During initiation of reaction, the temperature at the contact between an  $NH_4ClO_4$  particle and the smaller CC particles is the important kinetic temperature. This contact temperature will in general be less than the pellet surface temperature because of the temperature drop across a CC particle. The difference between the surface temperature and the contact temperature will be

greater, the greater the flux. This may be one reason that solid decomposition appears to be more important at high flux than at low flux. An additional factor may simply be the error involved in extrapolating Eq. (7) to high temperatures.

Even when the decomposition of  $\text{NH}_4\text{ClO}_4$  is unimportant thermally, decomposition may be important chemically. Kinetic experiments with AP/CC powder mixtures in the temperature range from 240 to 300°C revealed that the surface of the CC particles is chemically altered during the course of reaction. The reacted surface material rather than the original surface material may be the active material during ignition.

When ignition is not a consequence of a catastrophic rate of solid decomposition, the ignition process must depend on  $\text{NH}_3$  and  $\text{HClO}_4$ , the dissociation products of  $\text{NH}_4\text{ClO}_4$ . Of these,  $\text{HClO}_4$  is unstable at surface temperatures reached during ignition.<sup>20</sup> Decomposition will undoubtedly proceed more rapidly on some surfaces than in the adjacent gas. This would appear to be one plausible role played by CC during ignition, to promote the decomposition of  $\text{HClO}_4$  on the surface of the copper chromite particles. Even though reaction may begin on the surface of the copper chromite, it must spread eventually into the adjacent gas, and involve  $\text{NH}_3$  and  $\text{HClO}_4$  as gaseous species, as well as the products of the surface reactions. It is not clear why this process should result in measured exposure times that are independent of pressure.

#### B. AP/CC/C Ignition

Compared to AP/CC pellets, AP/CC/C ( $95/2\frac{1}{2}/2\frac{1}{2}$ ) pellets are unusually ignitable. In both cases, the minimum exposure time depends on the composition of the atmosphere in contact with the pellets. Consequently, in both cases ignition in  $\text{N}_2$  or A is probably controlled by gas phase or heterogeneous reactions involving normally gaseous species. Solid phase reaction may be involved but does not determine ignitability. These conclusions are consistent with the thermal history observations.

The ease of ignition of AP/CC/C pellets is reflected in the relatively low ignition temperatures in a  $N_2$  atmosphere. At the lowest value of  $\dot{q}_m$ , the calculated  $T_s$ , as well as the intercept temperature  $T_0$  at  $\dot{q}_m = 0$ , is considerably less than the ignition temperature observed during thermal history experiments. This contrasts with results for the AP/CC mixtures where the intercept  $T_0$  ( $N_2$  atmosphere) is about  $40^\circ\text{C}$  greater than the thermal history ignition temperature. The difference is presumably related to the pressure-dependence of  $\tau$  for AP/CC/C pellets. That dependence does imply that for AP/CC/C pellets  $T_0$  at low pressure is greater than that determined at high pressure.

Both the arc image data and the thermal history data indicate that there is a synergistic effect associated with the presence of both CC and C. Presumably, CC operates as before, by promoting surface reactions involving  $\text{HClO}_4$ . In that case, the equilibrium pressure of  $\text{HClO}_4$  (for  $P_{\text{NH}_3} = P_{\text{HClO}_4}$ ) at  $T_s$  calculated from AP/CC data provides a measure of the quantity of material required for CC to operate effectively. At  $340^\circ\text{C}$ , the intercept  $T_0$  from Fig. 3, this pressure is 1 mm Hg. For AP/CC/C pellets the intercept  $T_0$  is  $240^\circ\text{C}$  and the corresponding equilibrium  $P_{\text{HClO}_4}$  is about  $1 \times 10^{-2}$  mm Hg.<sup>1</sup> The cited decrease in  $T_0$  and the associated decrease in dissociation pressure suggest that the presence of carbon results in a concentration of  $\text{HClO}_4$  greater than would be the case in the absence of carbon. This would occur for example if C absorbs  $\text{NH}_3$  and permits the concentration of  $\text{HClO}_4$  to rise to a higher value, one at which CC can act effectively. The absorption of  $\text{NH}_3$  by C is a reasonable process in view of the high specific area of the material used ( $25 \frac{\text{M}^2}{\text{gm}}$ ). The sensitivity of  $\tau$  to pressure (see Fig. 4) at low pressure then implies a competition between absorption and escape into the gas phase. The CC promoted reaction may also be pressure-sensitive when proceeding at temperatures much less than those prevailing during the ignition of AP/CC mixtures. However, the thermal history measurements show that carbon alone can

cause ignition when conditions are favorable, though not as readily as CC and C together. Tentatively, then, one can assign to carbon three roles: (1) as a fuel, (2) as a reaction promoter in the same manner as CC, and (3) as an absorber of  $\text{NH}_3$ . The role as fuel is not in itself relevant to ignition but it does permit study over a wider range of pressures than would otherwise be the case. The role as reaction promoter (item 2) would be important in the absence of CC. Item (3) appears to be the critical one in AP/CC/C mixtures.

### C. Empirical Description of Ignitability Data

Whatever the details of the ignition process we found empirically that for a given propellant, pressure and atmosphere the measured quantities  $\tau$  and  $\phi_m$  and the derived quantity  $T_s$  are related to each other by expressions of these types:

$$(\tau)^{\frac{1}{2}} = a(\phi_m)^{-b} \quad (7)$$

$$(\phi_m \tau) = \frac{c}{\phi_m} + d \quad (8)$$

$$T_s = T_0 + k\phi_m \quad (9)$$

where  $a$ ,  $b$ ,  $c$ ,  $d$ ,  $T_0$ , and  $k$  are positive constants presumably related to the reactions which occur during ignition. These three expressions are mutually compatible only for the limiting case  $b = 1$ ,  $d = k = 0$ . Over a limited range of variation in  $\phi_m$ ,  $\tau$ , and  $T_s$ , with the usual experimental accuracy, each type of equation provides a satisfactory summary of data. The various constants can be related to each other and to the range of variation of  $\phi_m$ ,  $\tau$ , and  $T_s$ .

Expressions of type (7) are frequently used to summarize ignition data.<sup>8,9</sup> In general, it is found that  $0 < b < 1$ , often  $b \sim 3/4$  (Refs. 8, 9 and our data). An attempt has been made to relate "b" to reaction kinetics.<sup>6,9</sup> In the present case, the insensitivity of  $b$  to marked changes in ignitability indicates that such analysis is unreliable.

Equation (8), viewed simply as an empirical description, relates the energy requirement ( $\phi_m \tau$ ) to the absorbed flux and permits extrapolation to higher values of flux than actually used. The intercept "d" is then the minimum energy requirement for ignition by arc image radiation and can be used for purposes of comparison as a measure of ignitability at high  $\phi$ .

The derived surface temperatures in Eq. (9) are fictitious quantities. If, however, the ignition reactions involve substantial activation energies, the onset of reaction will be abrupt and occur in the vicinity of  $T_s$ . One can accordingly regard  $T_s$  as the temperature at which the rate of chemical reaction becomes important. Generally, the constant  $k$  will be positive. Heat released near or on the surface of the pellet will be partially dissipated by conduction into the solid. The degree of dissipation will depend on the temperature gradient at the surface. This gradient, in the absence of reaction, is proportional to the absorbed flux, and will therefore be a more effective sink the greater the flux. Correspondingly, ignition temperature must increase with increasing flux.

The temperature  $T_0$ , determined by linear extrapolation of  $T_s$  to zero flux, may be regarded as the minimum temperature at which reactions of the type responsible for ignition at higher flux can cause ignition. If new reactions occur as the flux is reduced to zero,  $T_0$  need not correspond to a real temperature at which chemical reaction becomes important. Equation (9) and specific values of  $T_s$  can, however, be useful in evaluating the importance of a given reaction rate (like that in Eq. (7)), and for calculating vapor pressure.

#### D. Conclusions

We found empirically that for each of our propellants the minimum time of exposure,  $\tau$ , to radiation required for ignition is insensitive to pressure at high pressure but does depend on the composition of the atmosphere in contact with the sample and that  $\tau(A) < \tau(N_2) < \tau(He)$ . These observations suggest that the thermal conductivity of the gas is the property responsible for the variation of  $\tau$  with gas composition.

At high pressures the quantities  $\tau$  and  $\dot{q}$ , the energy flux to which the sample is exposed, are related by expressions of these two types

$$\tau^{\frac{1}{2}} = a(\dot{q})^{-b}$$

$$(\dot{q}\tau) = \frac{c}{\dot{q}} + d$$

where  $a$ ,  $b$ ,  $c$ , and  $d$  are positive constants that depend on the propellant composition and on the nature and pressure of the atmosphere in contact with the sample. The quantities  $\tau$  and  $\dot{q}$  have also been used to calculate the propellant surface temperature in the absence of reaction at the end of the exposure time,  $\tau$ . For our conditions this surface temperature  $T_s$  varies with flux  $\dot{q}$  as shown by

$$T_s = T_0 + k\dot{q}$$

where  $T_0$  and  $k$  are constants that depend on propellant composition and on the nature and pressure of the atmosphere. It does not appear feasible to relate the constants  $a$ ,  $b$ ,  $c$ ,  $d$ ,  $T_0$ , and  $k$  to the reactions which occur during ignition.

Analysis of the experimental data in conjunction with supplementary kinetic information indicated that in an inert atmosphere the early stage of ignition of composite propellants based on  $\text{NH}_4\text{ClO}_4$  can be dominated by either gas phase or solid phase reactions, depending on the circumstances. By gas phase reactions we include heterogeneous reactions involving molecular species normally gaseous. When experimental circumstances favor gas phase ignition, the critical species is probably  $\text{HClO}_4$ ; the critical reaction, the decomposition of  $\text{HClO}_4$  on the surface of the propellant. The conditions which favor gas phase ignitions are a high pressure of a poorly conductive gas, and the presence in the propellant of materials like carbon and copper chromite which promote the critical reaction. When conditions do not favor gas phase ignition, the decomposition of  $\text{NH}_4\text{ClO}_4$  can be an important source of thermal energy.

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**Table I**

**EFFECT ON  $\text{NH}_4\text{ClO}_4$  PARTICLE SIZE ON IGNITABILITY OF  
PELLETS CONTAINING FIVE WT % COPPER CHROMITE**

$\text{NH}_4\text{ClO}_4$ Particle Size (microns)	Minimum Exposure Time (msec)
88 - 124	15
61 - 88	18
43 - 61	18½
< 43	18½
Mixture A	16½
Mixture B	16½

Atmosphere:  $\text{N}_2$

Pressure: 25 to 40 atm

Incident Peak Flux: 85 cal/cm<sup>2</sup> sec

Mixture A:                      61 - 88 $\mu$   $\text{NH}_4\text{ClO}_4$     50% by wt  
    43 - 61 $\mu$         "            25% by wt  
    < 43 $\mu$         "            25% by wt

Mixture B (Ref. 11):    74 - 105 $\mu$   $\text{NH}_4\text{ClO}_4$     50% by wt  
    43 - 74 $\mu$                 25% by wt  
    < 43 $\mu$                 25% by wt

**Table II**

**THE EFFECT OF COPPER CHROMITE CONTENT  
ON THE IGNITABILITY OF  $\text{NH}_4\text{ClO}_4$ -COPPER CHROMITE PELLETS**

Copper Chromite (wt %)	Pressure Range (atm)	Minimum Exposure Time (msec)
3	40	15
4	30 to 40	16½
5	25 to 40	16½

Atmosphere:  $\text{N}_2$

Incident Peak Flux: 85 cal/cm<sup>2</sup> sec

$\text{NH}_4\text{ClO}_4$ : Mixture A (see Table I)

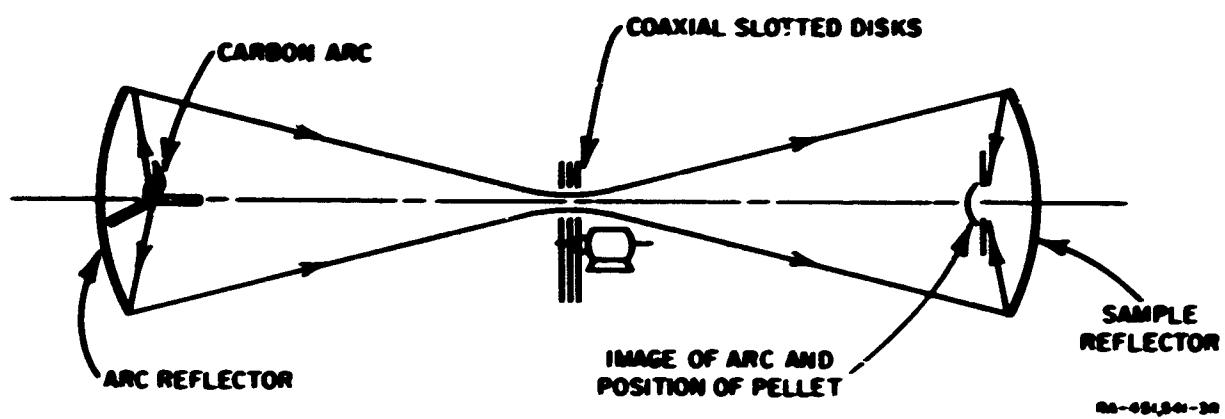


FIG. 1 SCHEMATIC DRAWING OF DOUBLE ELLIPSOIDAL CARBON ARC  
IMAGE SYSTEM

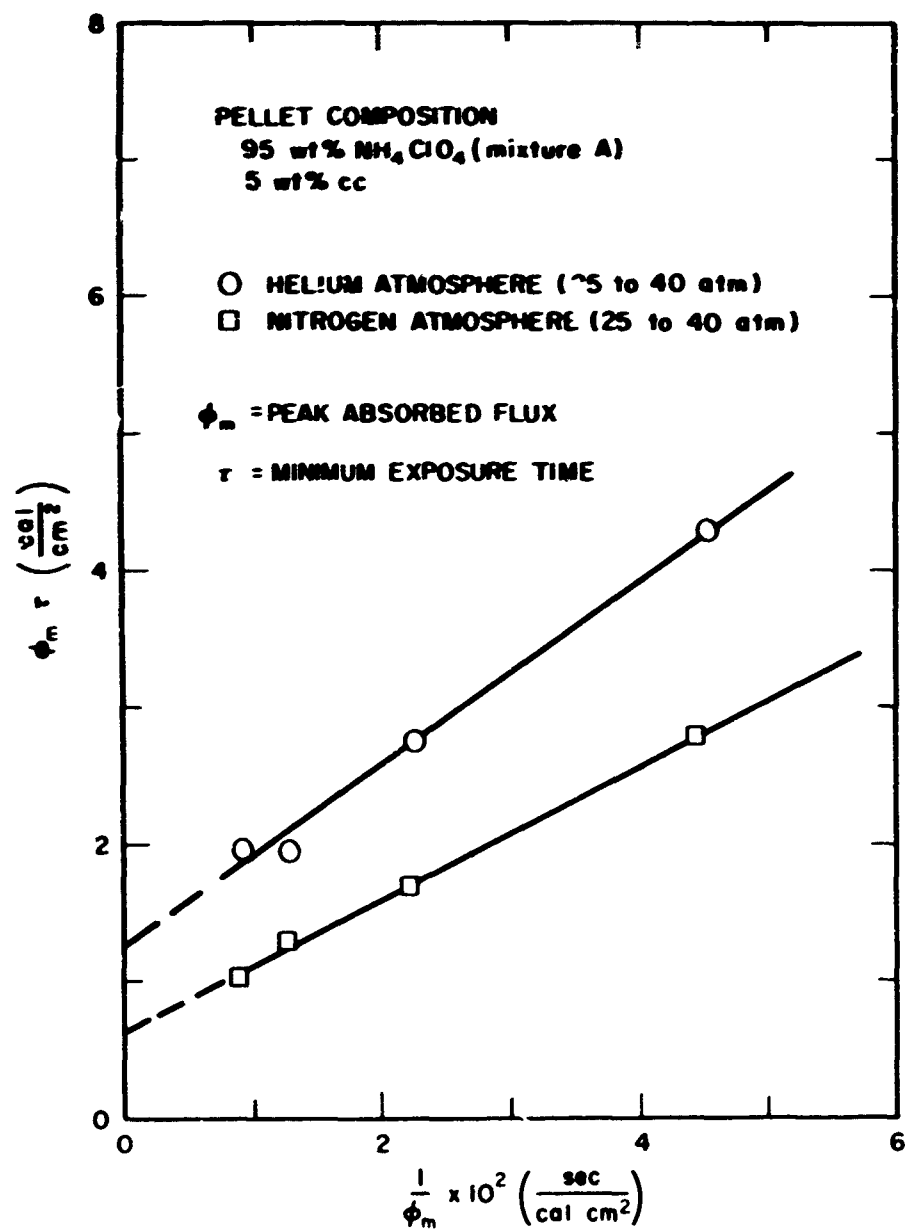
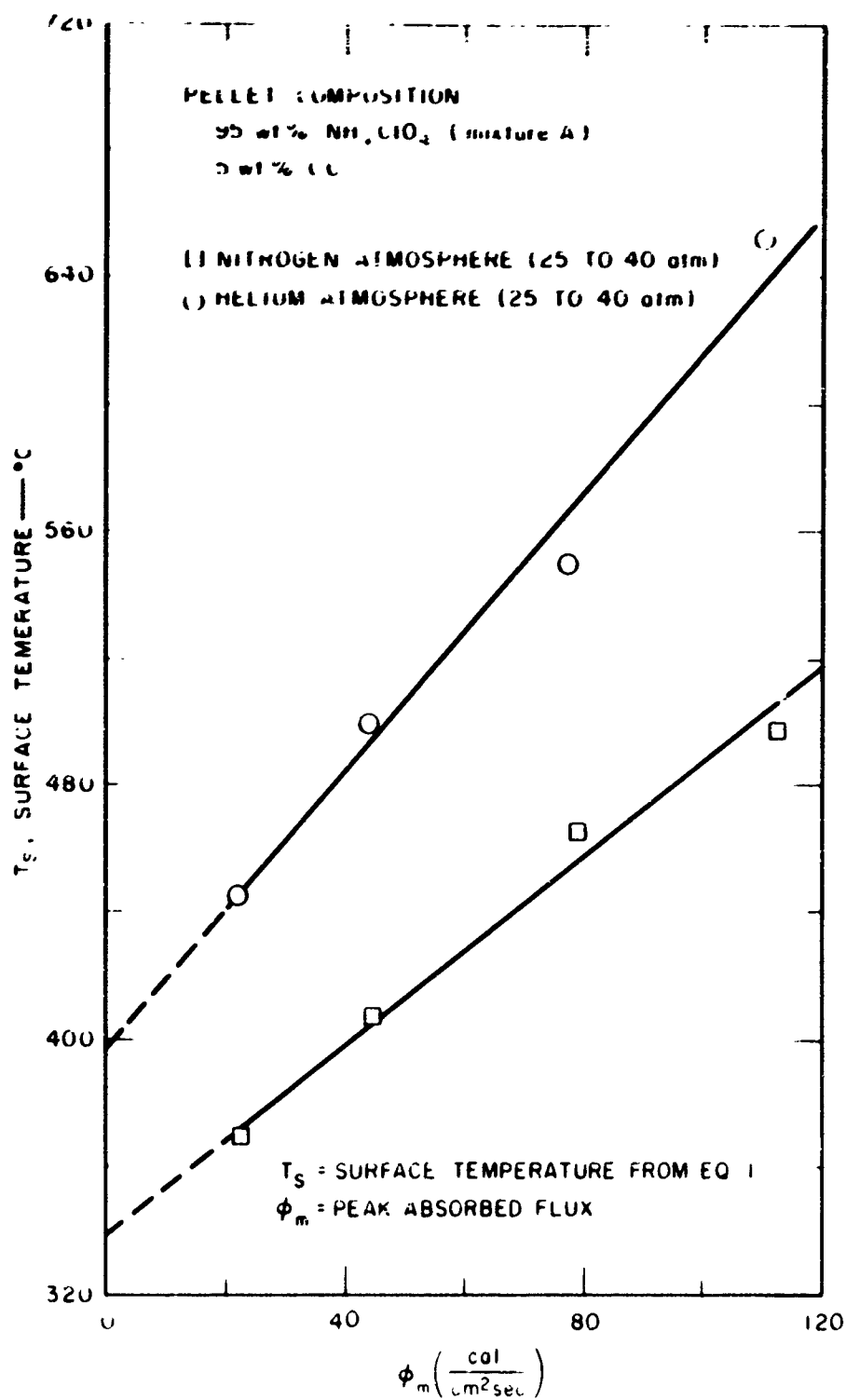
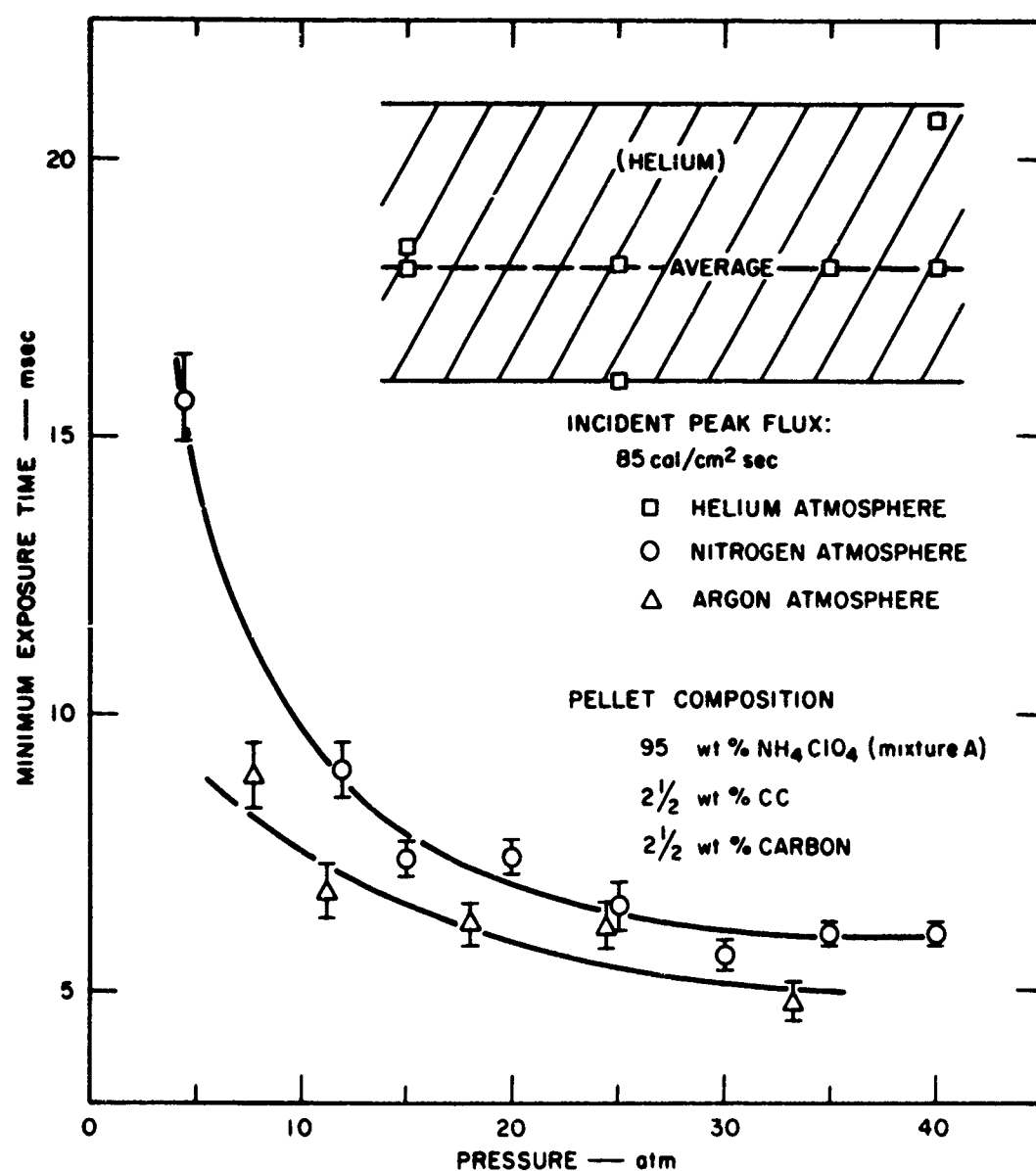


FIG. 2 THE EFFECT OF FLUX ON THE ENERGY REQUIRED TO IGNITE PELLETS OF  $\text{NH}_4\text{ClO}_4$  AND COPPER CHROMITE



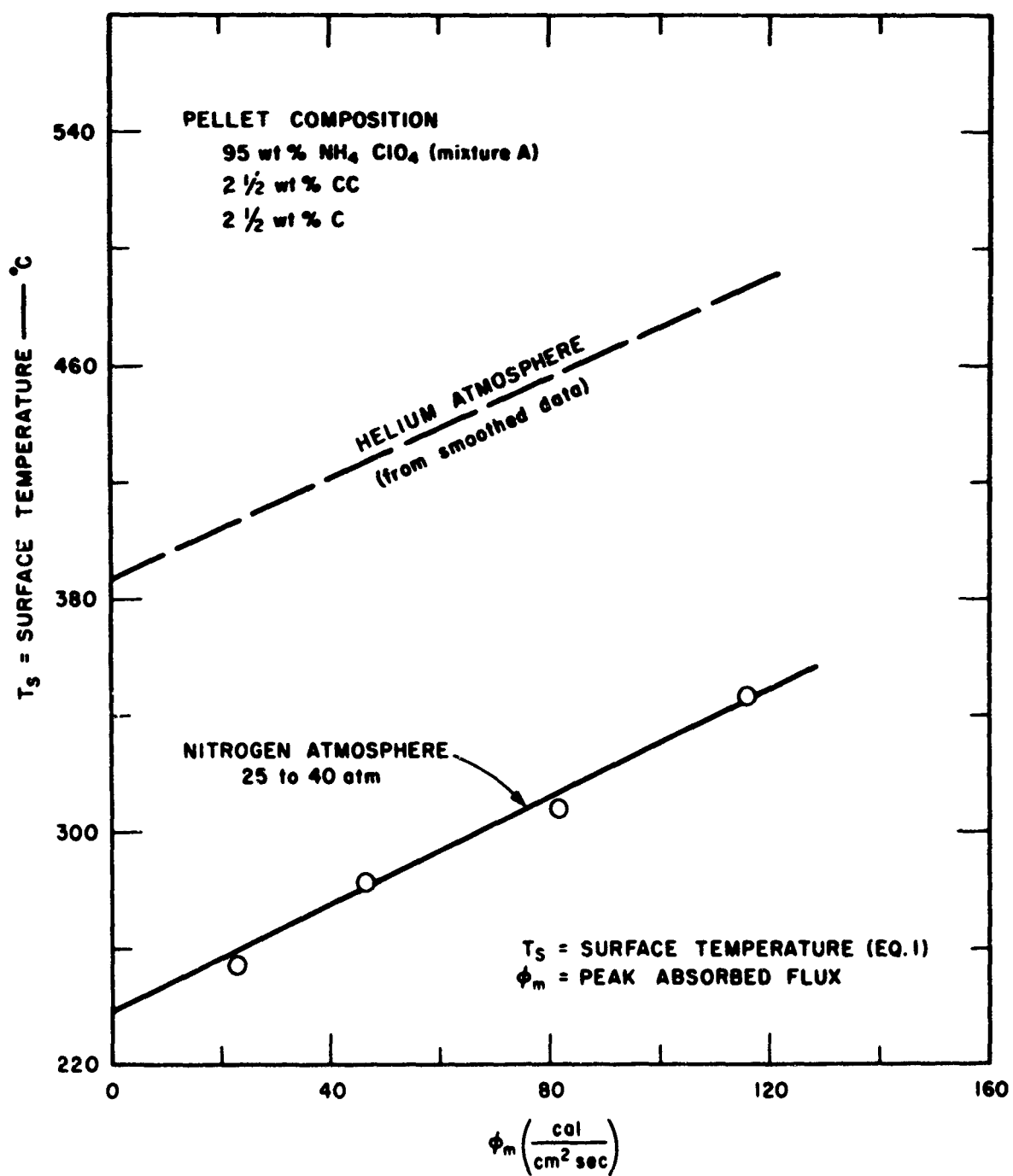
TA 3573 2

FIG. 3 THE EFFECT OF FLUX ON SURFACE TEMPERATURE:  
 $\text{NH}_4\text{ClO}_4$ /COPPER CHROMITE PELLETS



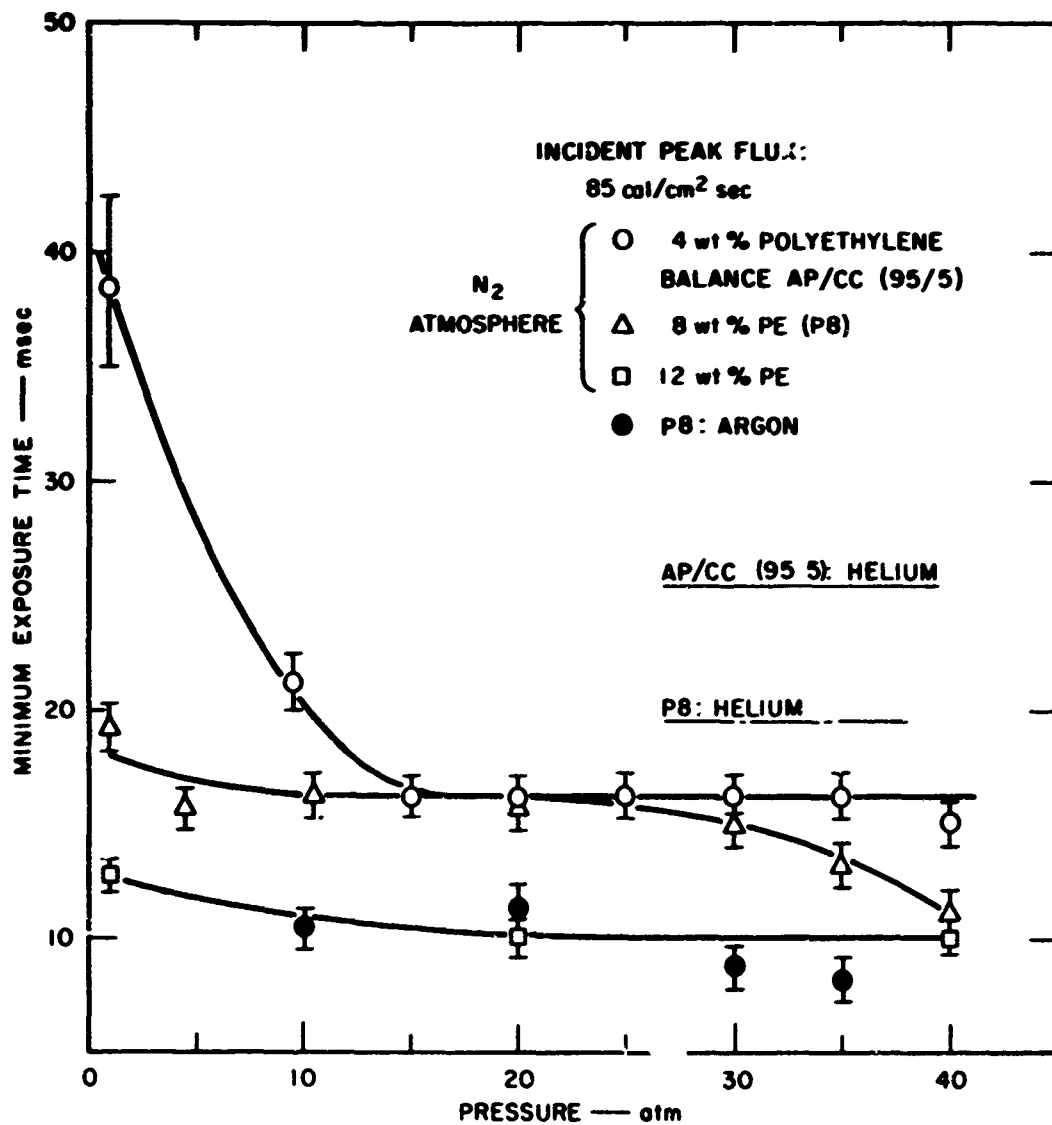
TR-3573-3

FIG. 4 THE EFFECT OF PRESSURE ON THE IGNITABILITY OF NH<sub>4</sub>ClO<sub>4</sub>/CARBON/COPPER CHROMITE PELLETS



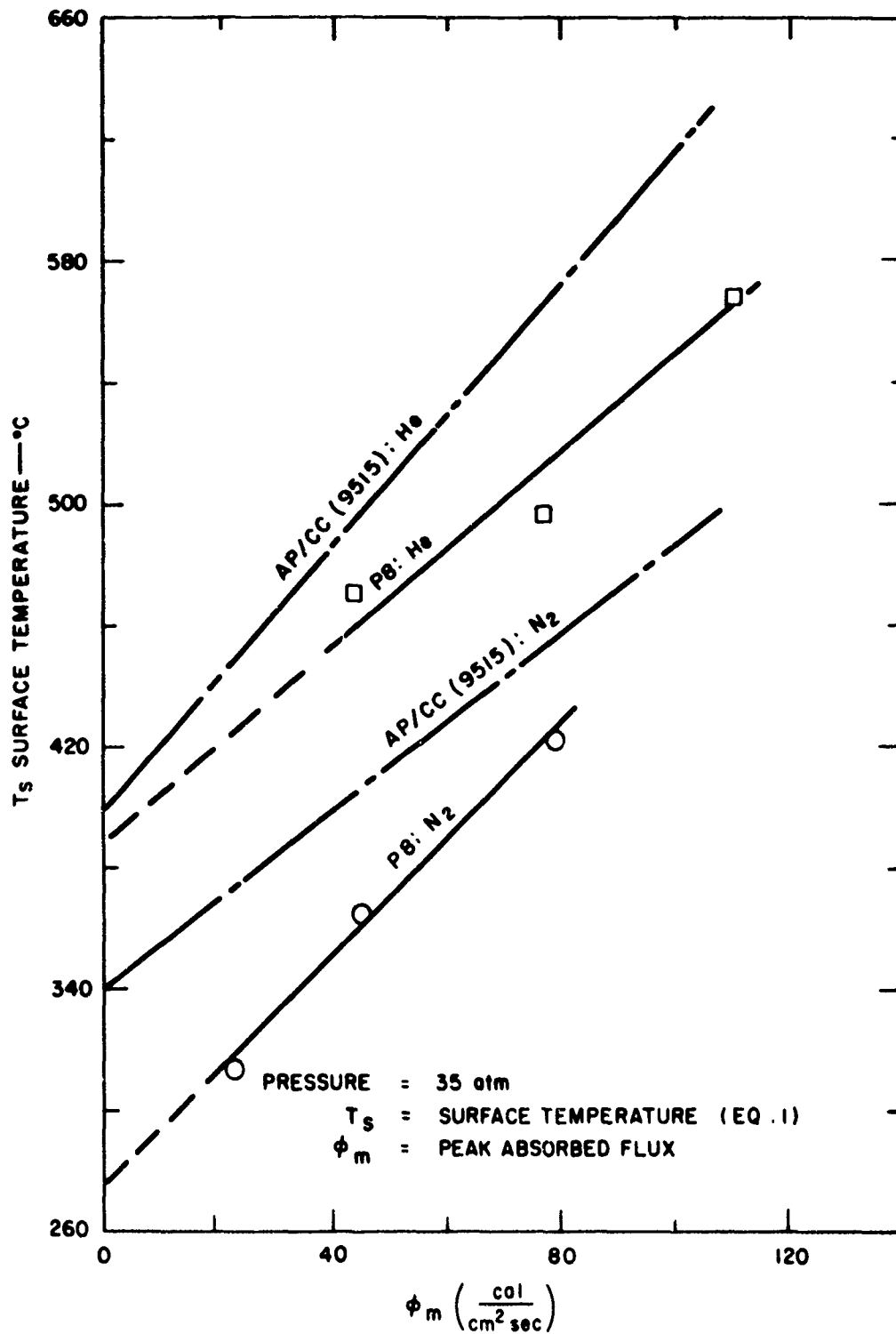
78-3573-4

FIG. 5 THE EFFECT OF FLUX ON SURFACE TEMPERATURE:  
 $\text{NH}_4\text{ClO}_4$ /COPPER CHROMITE/CARBON PELLETS



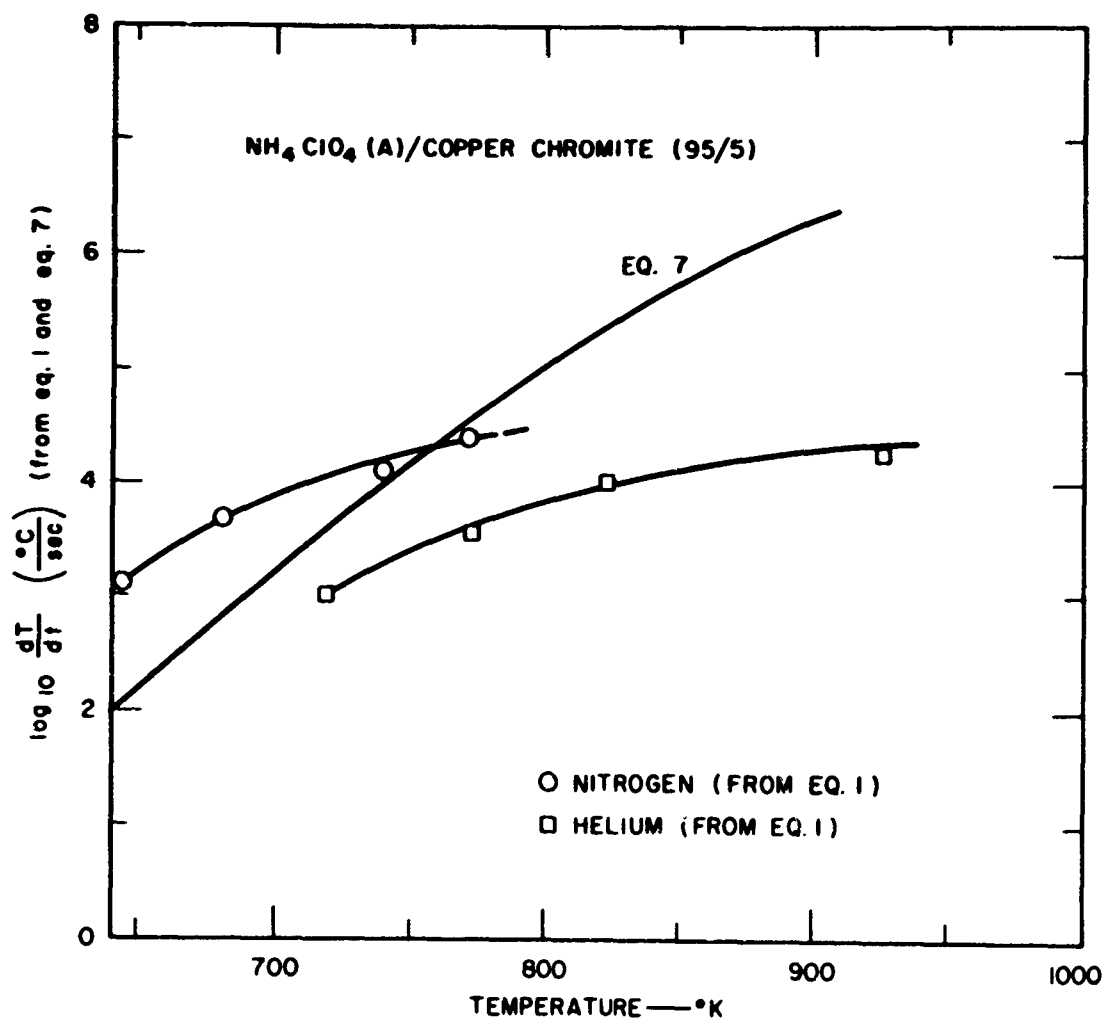
TB-3573-5

FIG. 6 THE EFFECT OF PRESSURE ON THE IGNITABILITY OF  
NH<sub>4</sub>ClO<sub>4</sub>/COPPER CHROMITE/POLYETHYLENE PELLETS



TA-5373-6

FIG. 7 THE EFFECT OF FLUX ON SURFACE TEMPERATURE:  
VARIOUS PELLET COMPOSITIONS



TA-3573-7

FIG. 8 COMPARISON OF ADIABATIC RATE OF DECOMPOSITION WITH RATE OF INCREASE OF SURFACE TEMPERATURE AT END OF EXPOSURE PERIOD: NH<sub>4</sub>ClO<sub>4</sub>/COPPER CHROMITE PELLETS